

Ionic Adsorption on the Surface of Hydroxides: A Molecular Dynamics Study

A.G. Kalinichev, J. Wang, and R.J. Kirkpatrick

Department of Geology

University of Illinois at Urbana-Champaign

Urbana, IL 61801 U.S.A.

Molecular dynamics computer simulations are performed to study thermodynamic and structural behavior of aqueous ionic solutions at the interface with $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, and typical mixed-metal layered hydroxides (MMLHs). MMLHs have a layered structure similar to that of $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$. However, due to the isomorphous substitution of +3 cations (often Al) for +2 cations (Mg or Ca) in the hydroxide layer, they develop a permanent positive layer charge. This charge is compensated by anions, which have associated water molecules, in the interlayer space and on the particle surfaces. MMLHs, also called layered double hydroxides (LDHs) and “anionic clays”, are among the few oxide-based materials with permanent anion exchange capacity. They occur in many natural environments, are readily synthesized, and are receiving rapidly increasing attention from a wide variety of applications as materials for catalysis, environmental remediation, and medicine. They also play a key role in cement chemistry, due to their importance in controlling the chemical behavior of anionic species.

The effects of temperature and water content on the molecular-level structural, energetic, and dynamic behavior of interlayer and surface species are investigated for bulk crystals and for the interfaces of hydroxide phases with aqueous solutions. A modified consistent valence force field was used to model all ion-ion and ion-water interactions. Molecular mechanisms of adsorption of aqueous Na^+ and Cl^- ions on the neutral $\text{Ca}(\text{OH})_2$ surface were studied in detail. The hydration energy of $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$ (hydrotalcite) was found to have a minimum at approximately $\text{Cl}/\text{H}_2\text{O} = 2$ ratio in the interlayer. The calculated diffusion coefficient of Cl^- as an outer-sphere complex on the positively charged surface of $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ (hydrocalumite) is almost three times that of inner-sphere Cl^- , but is still about an order of magnitude less than that of Cl^- in bulk aqueous solution at the same temperature. The mobility of the interfacial water molecules has also been investigated.